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Europäisches Patentamt
European Patent Office
Office européen des brevets

19

11 Publication number:

0 109 059
A1

12

EUROPEAN PATENT APPLICATION

21 Application number: 83111240.4

51 Int. Cl.: C 07 C 11/06, C 07 C 4/10,
B 01 J 29/28, B 01 J 29/38

22 Date of filing: 10.11.83

30 Priority: 10.11.82 IT 2415282
02.12.82 IT 2455082
27.01.83 IT 1929283
03.05.83 IT 2089683

43 Date of publication of application: 23.05.84
Bulletin 84/21

84 Designated Contracting States: DE FR GB IT

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54 Process for converting olefins having 4 to 12 carbon atoms into propylene.

57 A process for converting olefins having from 4 to 12 carbon atoms into propylene, wherein said olefins are contacted with an aluminosilicate having a crystalline and zeolitic structure and having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio equal to or lower than 300, at a space velocity higher than 50 kg/h of olefins per kg of pure zeolite and at a temperature of from 400 to 600°C, whereby said aluminosilicate is preferably selected from zeolites ZSM 5 and ZSM 11, and is used as such or in a modified form.

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PROCESS FOR CONVERTING OLEFINS HAVING 4 TO 12 CARBON
ATOMS INTO PROPYLENE

5 The invention relates to a process for converting olefins having 4 to 12 carbon atoms into propylene.

Nowadays, huge amounts of olefinic cuts from C_4^- to C_{12}^- , either linear or branched, are available throughout the world and they are widely employed for different purposes, 10 such as described e.g. in Italian patent publications 24152 A/82, 24550 A/82 and 19292 A/83.

15 Sometimes however, because of contingent reasons, even outside the chemical field such as for instance transportation difficulties, it would be better to have still further possibilities of use.

20 A promising use of said olefins would be their conversion into propylene and/or ethylene.

25 It is an object of the present invention to provide a process for converting olefinic cuts from C_4^- to C_{12}^- to propylene with a high yield of propylene and, optionally, also ethylene.

30 In its most general form, the invention relates to a process for converting olefins having 4 to 12 carbon atoms into propylene, which is characterized in that said olefins are brought into contact with an alumino-silicate having a crystalline and zeolitic structure and having a SiO_2/Al_2O_3 molar ratio (Z ratio) equal to or lower than 300, at space velocities higher than 50 kg/h of olefins per kg of pure zeolite and at temperatures of from 400 to 600°C, whereby said alumino-silicate is preferably selected 35 from zeolites ZSM 5 and ZSM 11, and is used as such or in a modified form.

Generally, the lower the Z ratio, the higher the space velocity; the examples show very good results correspon-

ding to a Z ratio of 28, but higher ratios are equally or more effective.

5 The catalyst comprises preferably zeolites of the ZSM type, as described e.g. in European patent publication 36707; best results were attained by using ZSM 5 or ZSM 11 zeolites in their acid form (H - ZSM 5 or H - ZSM 11), or in a modified form (for instance by means of phosphorus, 10 magnesium, calcium, strontium, barium, chromium, copper or zinc).

15 The modifying element can be incorporated into the catalyst by means of ion exchange or by other methods, for example impregnation or co-precipitation during the zeolite synthesis.

20 According to a particularly advantageous way for the preparation of a non-modified catalyst (e.g. H-ZSM 5), the raw product coming from the zeolite synthesis is dried, for instance at 120°C, calcined (e.g. at 540°C for some hours, in order to displace all the residual templating agent) and then exchanged with an aqueous solution of HCl, 25 NH₄Cl, NH₄NO₃ or an equivalent H⁺ or NH₄⁺ source. When an ammonium compound is used, it is necessary to heat, for instance at 400°C, in order to obtain the acid form. A survey of alternative techniques for the ion exchange is given e.g. in US patents 3,140,249; 3,140,251; 3,140,253 and in European patent publications 30796, 36707, 30 37168, 40463 and 68754. The zeolite, after calcination and conversion into the acid form, has a long life and a very high catalytic activity. The zeolites mentioned above can be used as catalysts (as such or in a modified form) 35 optionally in admixture with suitable amounts of oxides as binders, for instance SiO₂ or Al₂O₃. Other binders are disclosed e.g. in European patent publication 36707.

The regeneration of the catalyst can be carried out in air for some hours at 400 - 600°C. A steam regeneration

is described in European patent publication 36704 and according to a further and very successful method, the catalyst can be regenerated by a hydrogen treatment.

5

As to the initial activation of the catalyst, some methods are described in European patent publications 34444 and 35830; in general, it is advisable to activate the catalyst for some hours in air at 450 - 750°C (preferably at 10 540 - 700°C).

10

Any process for the conversion of olefinic cuts to propylene will be indicated hereafter as a "post-pyrolysis" process. When the raw material of a post-pyrolysis process is a 15 mixture of olefins having 4 C atoms, there is a considerable problem to be solved, because the C₄⁻ cuts always contain substantial amounts of paraffins in general also having 4 C atoms, which paraffins pass (at 400 - 600°C) the zeolite bed without taking part in any reaction.

20

Furthermore, a small amount of C₄ paraffins is produced by the post-pyrolysis process itself. The conversion to C₃H₆ could be enhanced by a recycle of the non-reacted C₄⁻ olefins or of the C₄⁻ olefins formed during the reaction. In such a case however, an increasing accumulation of n-butane and of isobutane would take place. This drawback could be avoided by separating paraffins from olefins before feeding the reactor, but such a separation is rather difficult. Butenes and isobutane cannot be isolated by a 25 simple distillation and it is usually necessary to carry out an extractive distillation (a troublesome technique) which is particularly difficult for the C₄⁻ cuts coming from catalytic cracking, where butane and isobutane may account for up to 50% of the whole. The problem however 30 can be solved in a surprisingly easy way by the process according to the invention, when employing an integrated oligomerization step. In other words, a particular embodiment of the invention (the feed being a paraffin-olefin mixture) comprises the following steps (reference is made 35

also to figure 1):

- 5 a) a preliminary oligomerization of a ($C_4^- + C_4^+$) mixture at a temperature of from 320 to 380°C, using a catalyst bed of zeolitic nature (see e.g. US patent No. 4,150,062) to obtain a mixture of olefins having from 5 to 8 C atoms, the C_4^+ paraffins remaining substantially unconverted;
- 10 b) cooling and condensation of the oligomerization effluent in order to separate the C_4^+ paraffins as a gaseous phase, and conversion of the remaining ($C_5^- - C_8^-$) mixture to propylene under the typical post-pyrolysis reaction conditions described above;
- 15 c) cooling the effluent from the reactor for the conversion to propylene and compression of said effluent, preferably at 13 - 16 absolute kg/cm², whereby the hydrocarbons having 4 or more C atoms are condensed and the hydrocarbons having less than 4 C atoms are separated as a gaseous phase.

These hydrocarbons ($< C_4$) can be advantageously fed to a conventional battery of distillation columns for thermal or catalytic cracking in order to recover all the propylene contained therein. The small amounts of aromatics (BTX) can be easily separated from the other $\geq C_4$ hydrocarbons, if necessary, and recycled together with the final ($C_4^- - C_8^-$) mixture, containing small amounts of butanes, produced during the conversion reaction described under item (b) above. In order to carry out the oligomerization, C_4^- olefins containing C_4^+ paraffins in any proportion, are initially brought into contact with a catalyst of zeolitic nature, for instance ZSM 5 or ZSM 11, in an acid or in a modified form, at 250 - 400°C (preferably 320 - 380°C) and at space velocities from 2 to 10 (preferably 4 - 8) kg/h of reactants per kg of pure zeolite (binder excluded). In other words, the olefins of the ($C_4^- + C_4^+$) mixture are converted almost totally into a ($C_5^- - C_8^-$) olefinic mixture, while butane and isobutane do not react. The

separation of the butanes can thus be carried out very easily by simple cooling with water at room temperature.

5 The olefinic (C_5^- - C_8^-) mixture liquifies while the butanes are separated as a gaseous phase, said (C_5^- - C_8^-) mixtures being optimal raw materials for the production of propylene. Depending on the working conditions during the synthesis of the zeolite, such as e.g. the dilution of the starting solutions, the zeolite crystallites may 10 have a widely variable size; in general, a sharp subdivision is noted at 0.5 - 1 μm , i.e. the crystallites' dimensions are generally above that level ("large size" crystals) or below that level ("small size" crystals). 15 The catalysts according to the present invention are preferably "small size" crystals and can e.g. be prepared according to the methods of US patent No. 3,926,782.

20 The following examples are given merely for illustrative purposes and do not in any way limit the scope of the invention.

Working conditions common to all the examples

25 a) Zeolite ZSM 5 was prepared according to example 24 of US patent 3,702,886 with stirring, so as to obtain crystallites having an average size below 0.5 μm ;

b) zeolite ZSM 11 was prepared according to US patent 3,709,979 with stirring, so as to obtain crystallites having an average size below 0.5 μm ;

30 c) the modified zeolites were obtained by ion exchange, unless otherwise specified in the tables;

d) all the catalysts were activated prior to use at 540°C for 2 hours, unless otherwise specified in the tables.

35 Examples 1 to 20

The zeolites, mixed with SiO_2 as a binder, were charged into a microreactor which was continuously fed at a pressure slightly higher than atmospheric pressure with a

5 mixture consisting of equal proportions (1:1) of 2-cis-butene and 2-trans-butene. The reaction conditions and results are given in table 1.

Example 21 (Regeneration Test)

10 After an 18-hour run according to example 20, the reaction was stopped and the catalyst was regenerated with air, at atmospheric pressure and at the reaction temperature (550°C) for 2 hours; feeding of butenes was started again according to the conditions of example 25 and after 1 hour the following results were obtained:

15	Conversion	88.60%
	Selectivity to iso C ₄ ⁻	8.62%
	Selectivity to C ₃ ⁻	38.50%
	Yield of iso C ₄ ⁻ + C ₃ ⁻	41.75%
	Selectivity to >C ₅	33.54%
20	Selectivity to saturated gases < C ₄	11.97%
	Selectivity to C ₂ ⁻	7.37%

Examples 22 to 44

25 0.5 g of zeolite, mixed with 0.21 g of Al₂O₃ as a binder, were charged into a microreactor which was continuously fed, at a pressure slightly higher than atmospheric pressure with an 0.7:1 (by moles) mixture of n-pentene-1 and helium. The reaction conditions and results are given 30 in table 2.

Examples 45 to 48

35 These examples were carried out according to the preceding examples, but pentene was substituted by n-hexene (examples 45 to 46) and n-octene-1 (examples 47 and 48), respectively. Data and results are given in table 3.

Examples 49 and 50

These examples were carried out according to examples 22

5 to 44, but pentene was substituted by an olefin fraction C₅, coming from a fluid bed catalytic cracking (FCC) and essentially consisting of hydrocarbons having 5 carbon atoms with approximately the following composition:

Olefins (C₅⁻) = 70% by weight;

10 Paraffins (C₅⁺) = 30% by weight;

Dienes < 0.5 by weight.

Data and results are given in table 3.

15 Examples 51 and 52

Examples 45 and 46 were repeated, substituting linear hexene by a branched isomer (2-methyl-1-pentene). Data and results are given in table 3.

20 It is apparent from the above that the cracking of branched olefins according to the present invention substantially leads to the same results as the cracking of the corresponding linear olefins. This is surprising in so far as 25 it was believed until now (see European patent publication 37,671) that linear olefins were far easier to convert in the presence of zeolites than the branched isomers.

Examples 53 to 60

30 3 g of H - ZSM 5 mixed with 0.9 g of SiO₂ as a binder, were loaded into a microreactor which was continuously fed with isobutene, at a pressure slightly higher than atmospheric pressure. Reaction conditions and results are 35 given in table 4.

These tests show the influence of the temperature on the reaction.

Examples 61 to 68

These tests were carried out by repeating example 55 (at 550°C) and varying the space velocity, i.e. the residence time. In this way it was possible to ascertain that for velocities up to about 311 h^{-1} , the increase in selectivity to C_3^- compensates at least partially the decrease suffered by the conversion in the long run. Data and results are indicated in table 4.

Examples 69 and 70

These tests were carried out by repeating example 65 and raising the temperature to 580°C. Data and the excellent results are indicated in table 4.

Examples 71 and 72

These tests were carried out by repeating example 55, employing a zeolite H - ZSM 5 with a much higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (204). The data and results given in table 4 show that the propylene yield was positively influenced by the increase in said ratio. However, if such ration increases excessively, a drastic reduction in the C_3^- yield occurs at higher space velocities.

Examples 73 and 74

These tests were performed by repeating example 57 and employing a zeolite activated for 2 hours at a higher temperature i.e. at 700°C; the reaction data are indicated in table 4 together with the excellent results which prove the positive influence exerted by the increase in the catalyst activation temperature.

Examples 75 and 76

These tests were carried out by repeating example 57 and

substituting the zeolite in the acid form by a zeolite partially exchange with Cr; the exchanged zeolite contained 5 0.8% by weight of Cr. Data and results are in table 4.

Examples 77 to 79

These tests were performed by repeating example 57 and substituting the zeolite in the acid form by a zeolite exchanged 10 with Mg. The tests prove that a modification with Mg exhibits excellent aspects (see table 4).

Examples 80 and 81 (Comparative Tests)

15 These tests were performed by repeating example 55 and reducing the space velocity to a very low value (3.5 h^{-1}). The low propylene yield clearly proves the importance of a velocity exceeding the critical value (50 h^{-1}); see table 4.

20 Example 82

PART A

As shown in figure 1, a reactor (A) was loaded with 10 g of 25 the H - ZSM 5 of example 1 and was then continuously fed, at 2 kg/cm² (absolute) and 350°C, with the 50/50 butenes mixture of example 1, the space velocity being 12.5 kg/h of butenes per kg of H - ZSM 5; the gaseous products were cooled and condensed (at 15°C), thus obtaining 61.1 g/h of 30 liquids and 63.9 g/h of gas. The gases contained 95.6 % by weight of isobutane, the rest being light olefins and paraffins ($\leq C_4$) and the liquids contained 99% by weight of a ($C_5^- - C_8^-$) mixture, the rest being aromatics.

35 PART B

The liquids obtained according to PART A were fed continuously to a second reactor (D) at 550°C and atmospheric pressure, the space velocity being WHSV = 65 h^{-1} ; said reactor had been loaded with 3.3 g of the same H - ZSM 5 of PART A. After a 4-hour run, the effluent from reactor (D)

had the following composition (% by weight):

5	C_2^+	0,39	$iso-C_4^-$	8,50	
	C_2^-	4,87	$C_5^- + C_6^-$	18,53	
10	C_3^+	6,44	Benzene	1,06	}
	C_3^-	31,88	Toluene	5,28	}
	C_4^+	4,06	Xylenes	6,16	BTX
	$n-C_4^-$	12,83			

Said effluent was used for the pre-heating of the feed stream (of reactor D) and was then compressed by (E) and cooled with condenser (F), resulting in:

- 15 a) a gaseous stream, rich in propylene, which can be rectified in (G), so as to recover C_3^- and, optionally also C_2^- ;
- b) a liquid stream, which can also be rectified - in (H) - so as to separate, if necessary, the very small amount of aromatics.

Example 83

PART B of example 82 was repeated, increasing the space 25 velocity to 128 h^{-1} ; after a 4-hour run the effluent from (D) had the following composition (% by weight):

30	C_2^+	0,34	$iso-C_4^-$	7,39	
	C_2^-	5,54	$C_5^- + C_6^-$	25,85	
	C_3^+	5,15	Benzene	1,03	}
	C_3^-	32,37	Toluene	4,72	BTX
	C_4^+	2,99	Xylenes	5,12	}
35	$n-C_4^-$	9,50			

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TABLE 1

EXAMPLE	1	2	3	4	5	6	7
<u>Operative conditions:</u>							
Catalyst	H-ZSM5(b)	See ex. 1	H-ZSM5	See ex. 4	H-ZSM11	See ex. 6	
SiO ₂ /Al ₂ O ₃ (moles)	28	"	28	"	82	"	
Amount of catalyst	(c)	"	3 grams (d)	"	see ex. 4	"	
Temp. (°C)	500	"	400	"	500	"	
Space velocity (a)	60	215	427	60	60	"	
Data survey after:	6 h	6 h	6 h	6 h	1 h	6 h	
<u>Results (%b.w.)</u>							
Conversion	88.58	80.05	74.55	91.11	87.64	88.45	86.03
Selectivity to iso-C ₄ ⁻	9.28	15.26	17.37	7.58	9.39	9.46	11.60
Selectivity to C ₂ ⁻	31.99	34.32	34.37	16.74	40.65	33.10	35.03
Yield (iso C ₄ ⁻ + C ₂ ⁻)	36.56	39.69	38.57	21.25	43.86	37.64	40.12
Sel. to compounds \leq C ₅	41.31	42.60	42.72	68.15	31.80	47.10	41.55
Sel. to saturated	13.19	5.64	4.32	5.52	10.80	11.95	8.09
Compounds \leq C ₄	4.22	2.28	1.73	1.02	7.37	4.39	3.73
Selectivity to C ₂ ⁻							

(a) WHSV (Weight Hourly Space Velocity) namely Kg/h of olefines per Kg. of pure zeolite (binder excluded);

(b)+30% b.w. SiO₂ (binder);

(c) depending on pre-fixed WHSV;

(d) 3 g of Zeolite+ 0.9 g of SiO₂.

TABLE 1 (Continuation)

EXAMPLE	8	9	10	11	12	13
<u>Operative conditions:</u>						
Catalyst	H-ZSM5	See ex. 8	H-ZSM5	H-P-ZSM5	H-ZSM5	See ex. 12
SiO ₂ /Al ₂ O ₃ (moles)	204	"	28	28	28	"
Amount of catalyst	see ex. 4	"	see ex. 4	"	see ex. 4	"
Temp... (°C)	550	"	500	"	550	"
Space velocity (a)	60	"	60	"	82	"
Data survey after:	1 h	6 h	1 h	"	1 h	6 h
<u>Results (%b.w.)</u>						
Conversion	88.02	84.26	93.11	80.97	86.42	83.33
Selectivity to iso-C ₄ ⁻	9.13	12.52	5.44	14.97	10.41	13.02
Selectivity to C ₂ ⁻	37.98	38.01	28.14	36.68	44.36	45.72
Yield (iso C ₄ ⁻ + C ₃ ⁻)	41.55	42.50	31.27	41.82	47.33	49.00
Sel. to compounds \leq C ₅	35.77	39.32	40.54	40.48	27.48	27.87
Sel. to saturated						
Compounds \leq C ₄	10.36	5.54	21.34	5.22	10.34	7.49
Selectivity to C ₂ ⁻	6.75	4.71	4.54	2.66	7.41	5.85

(a) WHSV (Weight Hourly Space Velocity) namely Kg/h of olefines per Kg. of pure zeolite (binder excluded);

(*) Zeolite H-P-ZSM5 was containing 3.17 b.w. of phosphorus; trimethyl-phosphite was added according to Vedral et. al. "J. Catal. 73, 147 (1982).

(**) Zeolite H-ZSM5 was activated 2 h at 700°C in air, before being used.

TABLE 1 (Continuation)

EXAMPLE	14	15	16	17	18	19	20
<u>Operative conditions:</u>							
Catalyst	Zn-ZSM5	Cr-ZSM5	See ex. 15	Cu-ZSM5	See ex. 17	See ex. 17	See ex. 19
$\text{SiO}_2/\text{Al}_2\text{O}_3$ (moles)	28	See ex. 14	"	"	"	"	"
Amount of catalyst	See ex. 4	"	"	"	"	"	"
Temp... (°C)	550	"	"	"	"	"	"
Space velocity (a)	60	"	"	"	"	"	"
Data survey after:	6 h	1 h	6 h	1 h	6 h	1 h	6 h
<u>Results (xb.w.)</u>							
Conversion	90.67	89.86	88.27	93.66	80.99	88.62	79.30
Selectivity to iso- C_4^-	6.88	7.50	8.88	4.45	15.56	8.74	16.66
Selectivity to C_2^-	32.10	37.34	38.57	26.48	43.42	38.83	42.13
Yield (iso $\text{C}_4^- + \text{C}_3^-$)	35.34	40.29	41.88	28.97	47.77	42.12	46.78
Sel. to compounds $\text{C}_4^- \text{ to } \text{C}_5^-$	46.62	34.39	35.81	47.94	28.73	34.70	30.41
Sel. to saturated							
Compounds $\leq \text{C}_4^-$	8.49	12.81	9.47	14.35	7.09	10.35	5.79
Selectivity to C_2^-	5.92	7.97	7.26	6.79	5.19	7.40	4.31

(a) WHSV (Weight Hourly Space Velocity) namely Kg/h of olefines per Kg. of pure zeolite (binder excluded);

TABLE 2

EXAMPLE	22	23	24	25	26	27	28	29
Operative Conditions:								
Catalyst	H-ZSM5	H-ZMS5						
SiO ₂ /Al ₂ O ₃ (moles)	26	28	"	"	"	"	"	"
Amount of catalyst (g)	(c)	(c)	"	"	"	"	"	"
Temp. (°C)	400	500	"	"	"	"	"	"
Space velocity (a)	71.4	71.4	"	142.8	"	550	"	585
Data survey after:	1 h	1 h	6 h	1 h	6 h	71.4	"	178.6
Results: (% b.w.)						71.4	1 h	6 h
Conversion	65.31	82.60	78.92	70.40	62.88	88.98	84.25	82.83
Selectivity to C ₂ ⁻	4.01	13.50	13.46	12.77	12.45	21.26	21.87	25.32
Selectivity to C ₃ ⁻	23.30	27.36	33.06	33.71	36.50	30.31	37.50	36.69
Yield (C ₂ + C ₃)	17.83	35.75	36.71	32.72	30.78	45.89	45.99	51.36
Sel. to saturated compounds < C ₄	2.94	8.20	5.04	4.33	2.77	6.46	3.11	2.36
Sel. to C ₄ ⁻	30.84	17.37	23.82	27.44	32.16	13.28	19.54	17.67
Sel. to C ₅ ⁺	12.00	12.41	8.78	7.36	5.23	6.81	4.01	2.47
Sel. to BX (b)	10.14	15.84	10.66	9.26	6.10	19.07	11.27	12.83
Sel. to other								
Liquids	17.27	5.20	5.22	5.31	4.90	2.79	2.60	1.93

(a) See ex. 1; (b) BX = benzene + toluene + xylenes; (c) 0.5 g of pure zeolite + 0.21 g of Al₂O₃ (binder).

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EXAMPLE	30	31	32	33	34	35	36
Operative Conditions:							
Catalyst	H-ZSM5	See ex. 30	(a)	(*)	(*)	(**)	(**)
SiO ₂ /Al ₂ O ₃ (moles)	28	"	H-ZSM5 see ex. 30	Cr-H-ZSM5 see ex. 30	See ex. 33	Zn-ZSM5	See ex. 35
Amount of catalyst	see ex. 23	"	"	"	"	26	"
Temp. (°C)	500	"	"	"	"	see ex. 23	"
Space velocity (a)	55.7	"	"	"	"	550	"
Data survey after:	1 h	6 h	6 h	?	?	71.4	"
Results (% b.b.)							
Conversion	81.08	77.69	65.78	77.55	75.59	89.10	81.10
Selectivity to C ₂ ⁻	12.56	12.71	11.28	12.70	12.49	20.71	21.69
Selectivity to C ₃ ⁻	28.71	32.85	34.93	32.04	34.77	25.02	29.89
Yield (C ₂ + C ₃)	33.46	35.40	30.40	34.70	35.87	40.75	41.83
Sel. to saturated compounds < C ₄	7.44	5.24	3.30	4.80	4.14	1.73	1.01
Sel. to C ₄ ⁺	19.31	24.86	34.14	25.07	25.77	11.66	15.65
Sel. to C ₅ ⁺	11.93	9.18	4.74	9.35	7.45	4.20	2.28
Sel. to BTX (b)	13.80	11.08	4.82	12.02	9.75	32.92	23.30
Sel. to other liquids	6.17	6.39	5.94	6.00	5.73	3.64	2.81

(a) See ex. 1; (b) BTX = benzene + toluene + xylenes; (c) Zeolite H-ZSM5 was activated 2 h at 600°C before being used;

(d) Zeolite H-ZSM5 was activated 2 h at 700°C.

(*) Chromium was added by means of a partial ion exchange.

(**) Zn was added by means of a complete ion exchange, as to occupy practically all the sites within the Zeolite.

TABLE 2 (Continuation)

EXAMPLE	37	38	39	40	41	42	43	44
<u>Operative Conditions:</u>								
Catalyst	Cr-ZSH5 See ex. 35	(**) See ex. 37	(**) See ex. 35	(**) See ex. 39	(**) See ex. 41	(**) See ex. 41	(**) See ex. 41	(****)
SiO ₂ /Al ₂ O ₃ (moles)	2/3	2/3	2/3	2/3	2/3	2/3	2/3	2/3
Amount of catalyst	11	11	11	11	11	11	11	11
Temp. (°C)	11	11	11	11	11	11	11	11
Space velocity (a)	11	11	11	11	11	11	11	11
Data survey after:	1 h	6 h	1 h	6 h	6 h	6 h	6 h	6 h
<u>Results (% b.w.)</u>								
Conversion	84.75	77.96	89.56	78.33	63.84	63.06	49.43	70.56
Selectivity to C ₂ ⁻	21.85	21.66	20.69	22.42	20.34	20.07	21.02	22.05
Selectivity to C ₃ ⁻	37.65	38.48	28.06	40.48	40.22	40.27	41.29	38.36
Yield (C ₂ + C ₃)	50.49	46.89	43.66	49.27	38.39	38.05	30.80	42.63
Sel. to saturated compounds < C ₄	3.47	3.46	4.36	2.48	1.28	0.96	0.77	2.84
Sel. to C ₄ ⁺	19.39	24.86	13.58	23.82	29.17	30.16	29.96	24.91
Sel. to C ₅ ⁺	4.01	2.28	4.00	1.80	1.74	1.20	0.89	2.86
Sel. to BTX (b)	10.98	7.87	25.69	6.34	4.60	4.41	3.42	7.22
Sel. to other								
Liquids	2.60	3.18	4.30	2.56	2.61	2.92	2.61	1.71

(a) See ex. 1 (b) BTX = benzene + toluene + xylenes.

(**) See ex. 35; (****) Na occupies 50% of the sites within the zeolite;

(****) See ex. 11.

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TABLE 3

EXAMPLE	45	46	47	48	49	50	51	52
<u>Operative Conditions:</u>								
Catalyst	H-ZSM5	(*)	(*)	(**)	(**)	(***)	(***)	(****)
SiO ₂ /Al ₂ O ₃ (moles)	28	See ex.45	"	See ex.45	"	See ex.49	H-ZSM5	See ex. 51
Amount of catalyst	see ex.23	"	"	"	"	"	28	"
Temp. (°C)	550	"	"	"	"	see ex. 23	see ex.23	"
Space velocity (a)	71.4	"	"	"	"	585	"	"
Data survey after:	1 h	6 h	1 h	6 h	7 h	178.5	214	550
<u>Results (% b.w.)</u>								
Conversion	97.46	96.90	100	100	54.81	64.85	100	100
Selectivity to C ₂ ⁻	14.49	13.14	16.97	14.27	21.13	24.09	12.49	14.49
Selectivity to C ₃ ⁻	31.18	45.14	27.33	32.81	41.63	36.70	41.96	41.84
Yield (C ₂ + C ₃)	44.51	56.47	44.30	47.08	34.40	39.42	56.45	56.33
Sel. to saturated compounds < C ₄	6.54	2.12	6.00	2.93	1.97	3.72	1.86	1.01
Sel. to C ₄ ⁻	15.99	19.71	12.62	18.04	18.21	15.28	17.36	16.04
Sel. to C ₄ ⁺	5.84	1.43	7.13	4.02	1.53	3.19	1.28	0.58
Sel. to C ₅ ⁺	11.81	3.42	16.13	10.83	10.29	13.26	6.97	6.14
Sel. to BTX (b)								
Sel. to C ₅	10.42	12.81	8.66	11.06	-	-	14.80	16.18
Sel. to others	5.69	2.26	5.13	5.67	5.20	3.90	2.68	3.72

(a) See ex. 1 (b) BTX = benzene + toluene + xylenes; (*) Feed = n-hexene-1; (**) Feed = n-octene-1; (*** Feed = C₅ cut from F.C.C., containing C₄⁺, C₄⁻ and dienes; (****) Feed = 2-methyl-pentene + He; olefine/He = 0.7:1 by moles;
 (*****) Feed = pure 2-methyl-pentene, without He as diluent.

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TABLE 4

EXAMPLE	53	54	55	56	57	58	59	60
<u>Operative Conditions:</u>								
Catalyst	H-ZSM5	See ex. 53	See ex. 53	See ex. 55	See ex. 53	See ex. 57	See ex. 53	See ex. 59
SiO ₂ /Al ₂ O ₃ (moles)	28	"	"	"	"	"	"	"
Amount of catalyst (b)	(b)	"	"	"	"	"	"	"
Temp. (°C)	597	"	550	"	500	"	450	"
Space velocity (a)	60	"	60	"	60	"	60	"
Data survey after:	1 h	5.30 h	1 h	4.30 h	1 h	4.30 h	1 h	6.15 h
<u>Results (Z.b.m.)</u>								
Conversion	92.4	91.6	91.2	85.5	92.0	83.6	91.6	90.0
Selectivity to C ₃ ⁻	24.2	32.2	22.0	26.2	14.0	16.4	12.0	13.0
Yield (C ₃ ⁻)	22.4	29.5	20.1	22.4	12.9	14.5	11.0	11.7
Sel. to C ₂ ⁻	6.74	8.46	4.95	2.95	2.35	1.84	1.64	1.33
Sel. to saturated compounds < C ₄	21.0	14.1	31.6	20.4	36.2	27.5	32.7	25.5
Sel. to compounds \geq C ₅	32.9	30.6	22.4	21.0	27.5	30.1	35.1	39.7
Sel. to linear butenes	15.2	14.6	19.0	29.4	20.0	24.2	18.7	20.5

(a) See ex. 1; (b) See ex. 4.

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TABLE 4 (Continuation)

EXAMPLE	61	62	63	64	65	66	67	68
<u>Operative Conditions:</u>								
Catalyst	(*)	(*)						
H-ZSM5	See ex. 61	"	See ex. 61	"	"	See ex. 61	"	See ex. 61
SiO ₂ /Al ₂ O ₃ (moles)	28	"	"	"	"	"	"	"
Amount of catalyst	(b)	"	"	"	"	"	"	"
Temp. (°C)	550	"	"	"	"	"	"	"
Space velocity (a)	470	"	296	"	"	216	"	"
Data survey after:	1 h	5 h	1 h	4 h	1 h	5.15 h	1 h	6 h
<u>Results (% b.u.)</u>								
Conversion	76.2	69.6	35.2	81.8	86.8	81.0	88.2	85.2
Selectivity to C ₃ ⁻	26.8	25.0	34.1	34.4	33.5	34.2	22.4	29.8
Yield (C ₃ ⁻)	20.4	17.4	29.1	28.1	29.1	27.7	19.2	25.4
Sel. to C ₂ ⁻	1.61	1.30	4.92	3.81	5.49	3.48	2.85	3.64
Sel. to saturated compounds < C ₄	14.4	8.57	16.6	11.4	19.9	11.0	26.2	14.6
Sel. to compounds $\geq C_5$	14.1	13.0	15.5	16.7	13.8	15.0	22.7	20.6
Sel. to linear butenes	43.1	52.0	28.8	33.7	27.4	36.2	25.8	31.4

(a) See ex. 1 (b) See ex. 4.

(*) Comparative examples; space velocity is too high and either conversion or selectivity to C₃⁻ decrease with the time.

TABLE 4 (Continuation)

EXAMPLE	69	70	71	72	73	74
Operative Conditions:						
Catalyst	H-ZSM5	See ex. 69	H-ZSM5	See ex. 71	H-ZSM5	See ex. 73
$\text{SiO}_2/\text{Al}_2\text{O}_3$ (moles)	28	"	204	"	28	"
Amount of catalyst (b)	"	"	"	"	(b)	"
Temp. (°C)	580	n	550	"	500	"
Space velocity (a)	216	"	60	"	60	"
Data survey after:	1 h	5.15 h	1 h	5.30 h	1 h	6.30 h
Results (% b.w.)						
Conversion	88.8	84.1	87.7	83.6	86.87	85.19
Selectivity to C_3^-	39.3	39.9	42.7	44.8	31.96	31.97
Yield (C_3^-)	34.9	33.6	37.5	37.4	27.76	27.24
Sel. to C_2^-	8.64	6.68	8.39	6.30	4.32	3.42
Sel. to saturated compounds < C_4	16.0	10.0	17.4	10.7	19.31	14.60
Sel. to compounds $\geq \text{C}_5$	15.0	15.4	10.2	10.4	20.31	23.33
Sel. to linear butenes	21.0	28.1	21.4	27.8	24.10	26.28

(a) See ex. 1; (b) See ex. 4.

(*) Zeolite H-ZSM5 was activated 2 hours at 700°C before being used.

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TABLE 4 (Continuation)

EXAMPLE	75	76	77	78	79	30	61
<u>Operative Conditions:</u>							
Catalyst	C ₁ -H-ZSM5	See ex. 75					
SiO ₂ /Al ₂ O ₃ (moles)	28	"					
Amount of catalyst (b)		"					
Temp. (°C)	500	"	"	"	"		
Space velocity (a)	60	"	"	"	"		
Data survey after:	1 h	6 h	1 h	6.30 h	12 h	1 h	5.30 h
<u>Results (% b.u.)</u>							
Conversion	90.26	88.69	89.86	88.20	86.40	91.6	90.0
Selectivity to C ₃ ⁻	25.44	29.49	26.66	29.55	32.65	12.0	13.0
Yield (C ₃ ⁻)	22.96	26.15	23.98	26.15	26.21	11.0	11.7
Sel. to C ₂ ⁻	4.84	4.63	4.83	4.32	4.01	4.01	3.42
Sel. to saturated compounds < C ₄	25.50	17.78	26.72	18.94	15.88	46.0	37.3
Sel. to compounds \geq C ₅	25.38	27.52	22.61	25.76	23.92	40.8	50.3
Sel. to linear butenes	18.83	20.58	19.18	21.34	23.54	3.0	3.0

(a) See ex. 1; (b) See ex. 4.

(*) Comparative examples.

CLAIMS

1. A process for converting olefins having from 4 to 12 carbon atoms into propylene, characterised in that said olefins are contacted with an alumino-silicate having a crystalline and zeolitic structure and having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio equal to or lower than 300, at a space velocity higher than 50 kg/h of olefins per kg of pure zeolite and at a temperature of from 400 to 600°C, whereby said alumino-silicate is preferably selected from zeolites ZSM 5 and ZSM 11, and is used as such or in a modified form.
2. The process of claim 1, wherein the crystallites of said alumino-silicates have an average size equal to or lower than 0.5 μm and are selected from ZSM 5 and ZSM 11 zeolites, in which the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is from 13 to 220, preferably from 25 to 220.
3. The process of claim 1 or 2, wherein the space velocity is from 60 to 300, preferably from 60 to 250 h^{-1} .
4. The process of any of claims 1 to 3, wherein the zeolites are activated in air, before being used, at a temperature of from 450 to 750, preferably of from 540 to 700 °C.
5. The process of any of claims 1 to 4, wherein the zeolites are periodically regenerated with air at a temperature of from 400 to 600°C.
6. The process of any of claims 1 to 5, wherein the zeolites are admixed, before being used, with a binder, preferably selected from SiO_2 and Al_2O_3 .
7. The process of any of claims 1 to 6, wherein the zeolites are used in their acid form.

8. The process of any of claims 1 to 7, wherein said olefins are selected from isobutene, n-butenes and mixtures of olefins having 5 to 8 carbon atoms.
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9. The process of any of claims 1 to 8, wherein the zeolites are used in a modified form with the modifying elements being selected from Mg, Ca, Sr, Ba, P, Cr, Cu, 10 Zn and mixtures thereof.
10. A process for the conversion into propylene of mixtures of olefins having 4 C atoms, said mixtures containing also C_4^+ paraffins that cannot be easily separated from olefins, which process comprises the following steps:
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a) preliminary oligomerization of a $(C_4^- + C_4^+)$ mixture at a temperature of from 320 to 380°C in a catalyst bed of zeolitic nature to obtain a mixture of olefins having from 5 to 8 C atoms, with the C_4^+ paraffins remaining unconverted;
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b) cooling and condensation of the oligomerization effluent in order to separate the C_4^+ paraffins as a gaseous phase, and conversion of the remaining $(C_5^- - C_8^-)$ mixture to propylene under the reaction conditions of claim 1;
25
c) cooling the effluent from the reactor for the conversion to propylene and compressing said effluent, preferably at 13 - 16 absolute kg/cm², whereby the hydrocarbons having 4 or more C atoms are 30 condensed and the hydrocarbons having less than 4 C atoms are separated as a gaseous phase.
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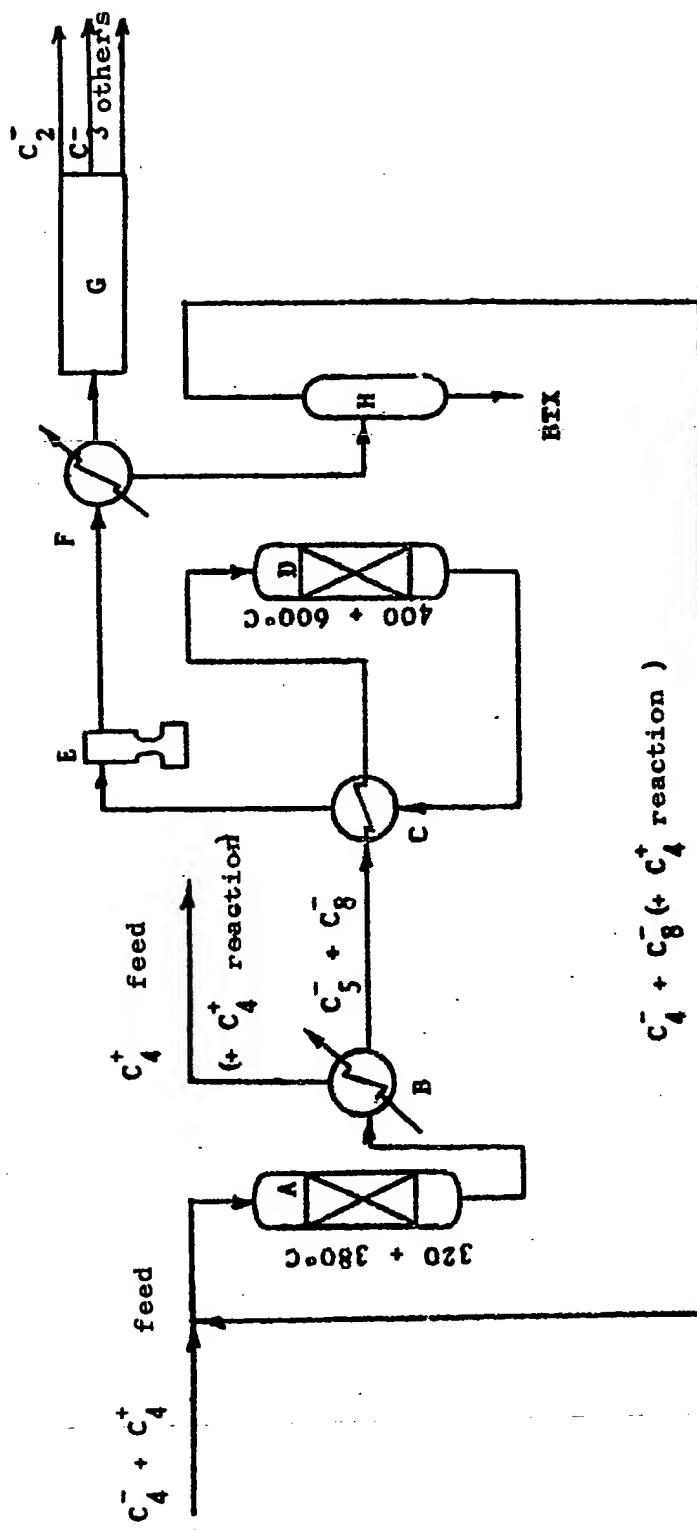


FIGURE 1



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 5)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	EP-A-0 037 671 (MOBIL OIL CORP.) * Page 11, paragraph 2; page 17, paragraphs 1-2; claims *	1, 2, 4, 6	C 07 C 11/06 C 07 C 4/10 B 01 J 29/28 B 01 J 29/38
A, D	EP-A-0 036 704 (MOBIL OIL CORP.) * Claims *	5	
A, D	US-A-4 150 062 (GARWOOD et al.) * Examples 5-6; claims *	10	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 5)
			C 07 C 11/00 C 07 C 4/00
<p>The present search report has been drawn up for all claims</p>			
Place of search THE HAGUE	Date of completion of the search 30-01-1984	Examiner VAN GEYT J.J.A.	
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>	
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p>			